Indian Journal of Chemistry
Vol. 36B, March 1997, pp. 246-251

Alkylation of aromatic substrates with methanol on heteropolyoxometalate

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Received 5 December 1995; revised and accepted 7 October 1996

The alkylation of aromatic substrates with methanol has been studied on potassium substituted salts of 12-phosphotungstic acid. Substitution at ring positions appears to be the predominant route. Among the potassium substituted salts, the salt containing $K_{2.5}$ is the most active probably because of higher strength of Bronsted acid sites on this system. Mechanistic details of this reaction are discussed.

The studies on the catalytic alkylation of aromatic hydrocarbons are related to the elucidation of mechanistic aspects and to the use of this reaction as a probe for establishing shape selectivity[1,2]. Though majority of the published results deal with the mechanism of the process on zeolites[1-10], still details are not completely understood. It is generally considered that acidic sites are responsible for the alkylation at the benzene ring[3] and side chain alkylation occurs on basic sites[5-7]. A number of studies[11-14] have dealt with shape selective aspects of the alkylation process. Okuhara and coworkers[15] have studied the alkylation of toluene on phosphotungstic acid and its sodium salt. Nishi and coworkers[16] studied alkylation of toluene on the ammonium salt of phosphotungstic and silicontungstic acids and have shown the operation of shape selectivity.

The present paper deals with the studies on the alkylation of toluene and other polyalkylbenzenes as well as the dealkylation of different polyalkylbenzenes on potassium salt of phosphotungstic acid ($K_xH_{3-x}PW_{12}O_{40}$). The scope of present investigation includes study of the mechanistic aspects of toluene alkylation and also evaluation of product selectivity, especially selectivity of *p*-xylene as a function of x in $K_xH_{3-x}PW_{12}O_{40}$.

Materials and Methods

12-Tungstophosphoric acid ($H_3PW_{12}O_{40}$) and 12-tungstosilicic acid ($H_4SiW_{12}O_{40}$) were prepared by the procedure reported in literature[17]. $K_xH_{3-x}PW_{12}O_{40}$ (K_x) was prepared by the addition of a solution containing stoichiometric amount of potassium carbonate to an aqueous solution of the parent acid. The resulting mixture was evaporated to dryness on a water-bath and then dried overnight at 373 K in a hot air oven. The parent acid supported on silica gel (80-100 mesh, surface area 440 m^2/g) was prepared by wet impregnation method. All the catalysts were characterised by IR, TGA, DSC, XRD methods. All the organic reagents employed were of high purity and were used as such. Xylenes and toluene (99%) of BDH grade and trimethylbenzene (99%) and tetramethylbenzene (99%) of Fluka grade were used.

Catalytic reactions were carried out in a fixed bed reactor working at atmospheric pressure. Various quantities and concentrations of two component solutions of aromatics and methanol were injected into the preheating zone at various controlled flow rates using a syringe infusion pump (Electronic Engineering Corporation, India). The reactant mixture was vaporised at the preheating zone before entering the reactor (20 mm internal diameter and 30 cm length). The catalyst was kept in the reactor supported with the help of quartz wool. The temperature of the catalyst bed was maintained using a thyeistor based temperature controller (Indian Furnaces, India) and was measured using a thermocouple placed at the centre of the catalyst bed.

The products were collected in a cold trap maintained at ice temperature and identified by GC-MS (Shimadzu, QP1000 EX). Quantitative analysis of the liquid products was carried out using Gas Chromatography (Chemito, Toshniwal, India) with SE30 column (1/8 in. dia, 3 metres length). In all the experiments, the catalysts used

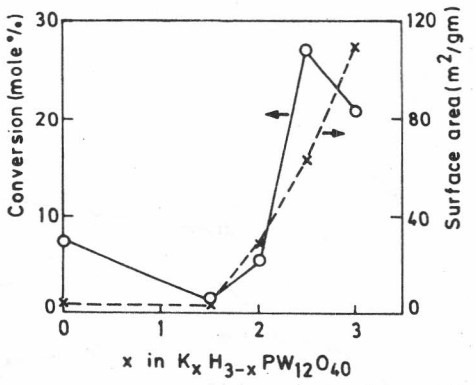


Fig. 1—Alkylation of toluene on $K_xH_{3-x}PW_{12}O_{40}$ [Temperature; 473 K, methanol : toluenel 1 : 1, W/F = 51.8 g hr/mole]; (○ conversion of toluene, × surface area of the catalyst)

were pretreated in nitrogen atmosphere at 650 K for 4 hr.

Results and Discussion

The major products obtained from the alkylation of toluene were xylenes and tri- and tetramethylbenzenes. Small amounts of benzene and pentamethylbenzene are also formed at higher temperatures. The variation of catalytic activity and surface area of $K_xH_{3-x}PW_{12}O_{40}$ as a function of x is shown in Fig. 1. Conversion of toluene shows a maximum when x = 2.5. The surface area of the system increases as potassium content increases. These results are consistent with the earlier reports[18] on the alkylation of 1,3,5-trimethylbenzene with cyclohexene on $Cs_{2.5}$ salt. It has been reported that[19] $Cs_{2.5}$ shows pronounced catalytic activity especially for the surface type reactions. For Cs salts, the catalytic activity correlates linearly with the surface acidity[20]. The fact that the conversion of toluene shows a maximum at x = 2.5 as in the case of $Cs_{2.5}$, suggests that the surface acidity of $K_xH_{3-x}PW_{12}O_{40}$ reaches maximum when x = 2.5 and conversion of toluene correlates linearly with the surface acidity of the catalyst.

The change in product selectivity with increasing potassium content is shown in Fig. 2. The selectivity of xylene decreases as the potassium content increases and passes through a minimum at x = 2.5. Selectivity of trimethylbenzene increases with increasing potassium content and shows a maximum at x = 2.5. Selectivity of tetramethylbenzene increases steadily at x > 2. The selectivity of benzene remains almost constant throughout the composition range. It is of interest to comment on the selectivity pattern of the xylene isomers formed during toluene alkylation. The data on selectivity of xylene isomers as a function of x in $K_xH_{3-x}PW_{12}O_{40}$ are given in Table I. It is observed that for all compositions the selectivity for *p*-xylene is higher than the equilibrium values[1]. As the potassium content increases the selectivity of *p*-xylene increases and shows a maximum at x = 2.5. It has to be noted that there is no direct correlation between conversion of toluene and *para* selectivity. This is in contrast to the results obtained with shape selective ZSM-5 type zeolites[2]. Yashima and coworkers[5,6] have reported that, in the case of Y zeolite, *p*-xylene formation

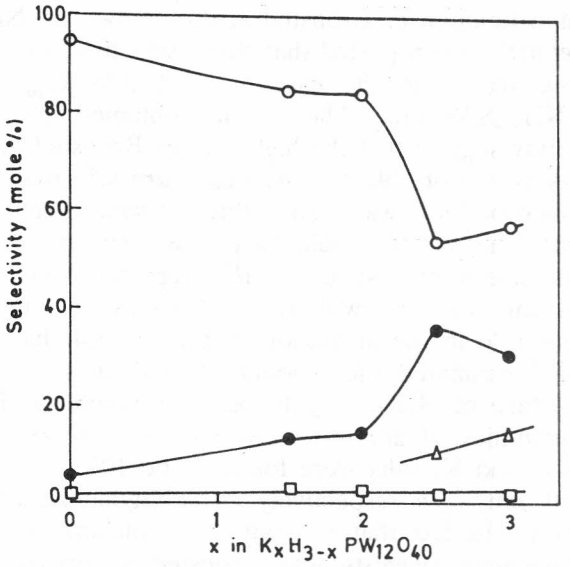


Fig. 2—Product selectivity in alkylation of toluene on $K_xH_{3-x}PW_{12}O_{40}$ [Temperature; 473 K, methanol : toluene; 1 : 1, W/F = 51.8 g hr/mole]; (○ xylene, ● trimethylbenzene, Δ tetramethylbenzene, □ benzene)

Table I—Selectivity of xylene isomers in the alkylation of toluene [toluene : methanol; 1 : 1, W/F; 51.8 g hr/mole, Temperature; 473 K]

Catalyst	Conversion (mole %)	Selectivity of xylene isomers (%)		
		p	*m*	*o*
$K_{1.5}H_{1.5}PW_{12}O_{40}$	2.2	39.2	39.2	21.5
$K_2HPW_{12}O_{40}$	6.6	51.5	30.4	18.0
$K_{2.5}H_{0.5}PW_{12}O_{40}$	26.9	54.3	31.2	14.5
$K_3PW_{12}O_{40}$	21.4	33.0	14.6	52.4
20 HPTA/SiO_2	7.8	30.1	21.8	48.0
20 HSTA/SiO_2	7.6	31.5	20.6	47.9
Equilibrium composition[1] at 500K		24.1	54.8	21.2

is a function of Bronsted acidity. However, Nishi *et al.*[16] have reported that shape selectivity may be the reason in the case of $(NH_4)_3PW_{12}O_{40}$ and $(NH_4)_4SiW_{12}O_{40}$. The results obtained in this study suggest that the high surface Bronsted acidity is responsible for the high *para* selectivity. If microporosity was responsible for *para* selectivity, then the K_3 salt should have shown maximum *para* selectivity. Nishi *et al.*[16] reported that the strong acid sites with $H_0 = -5.6$ play an important role in the alkylation of toluene. Okuhara *et al.*[18] estimated the amount of acid sites on the surface of $H_3PW_{12}O_{40}$ to be 8-16 μmoles/g. The quantities of acid sites (with $H_0 = -5.6$) on K_2, $K_{2.5}$ and K_3 salts were found to be 107, 135 and 59 μmoles/g respectively by *n*-butylamine titration. The fact that $K_{2.5}$ salt shows maximum *para* selectivity suggests that Bronsted acidity is responsible for *para* selectivity. This argument is further supported by the fact that 20% $H_3PW_{12}O_{40}/SiO_2$ (surface area 310 m^2/g) and 20% $H_4SiW_{12}O_{40}/SiO_2$ (surface area 306 m^2/g) show high *ortho* selectivity (Table I) due to low acid site density obtained by high dispersion of acid sites on the high surface area silica.

The adsorption centres in heteropolyoxometalates have been recognised as Bronsted acid sites[15,19,21]. Adsorbed methanol and aromatic molecules can be normally found predominantly around these sites. The extent of interaction depends on the acid strength and density of the sites and the basicity of the molecules[22]. Since the alkylation reaction proceeds through Rideal-Eley[4] mechanism, the adsorbed alcohol as a carbonium ion interacts with the organic substrate. It has been reported that catalyst systems with high acid strength and density yield *para* alkylated products preferentially. However, on less acidic systems the substitution at *ortho* position is more favoured[10]. Steric limitations of the interaction of the carbonium ion with organic substrates may account for the observed *para* selectivity.

The effect of temperature on the conversion and selectivity in toluene alkylation on $K_3PW_{12}O_{40}$ is shown in Fig. 3. The conversion of toluene increases with the increase in temperature and reaches a maximum. With the increase in temperature, selectivity for xylene passes through a minimum while selectivities of *tri-* and *tetra*-methylbenzenes pass through a maximum. The selectivity of benzene increases with the increase in temperature. These results are similar to those reported earlier on $(NH_4)_3PW_{12}O_{40}$ and $(NH_4)_4SiW_{12}O_{40}$ (ref. 16).

The data on the effect of contact time on the conversion and product selectivity at various temperatures are given in Table II. Conversion of toluene increases with the increase in contact time. Selectivity of xylene decreases with increasing contact time and passes through a minimum whereas the selectivities of both *tri-* and *tetra*-methylbenzenes increases with the increase in contact time and pass through a maximum. The data suggest that alkylation of benzene ring is a consecutive process. It has been proposed by Nishi *et al.*[16] that the polyalkylation of xylene is a faster process as compared to the alkylation of toluene. The data on selectivity with respect to xylene isomers are also given in Table II. It is seen that selectivity with respect to *para* isomer decreases as a function of contact time. It is also inferred that the alkylation of toluene is slower than those of xylenes and higher alkylated benzene.

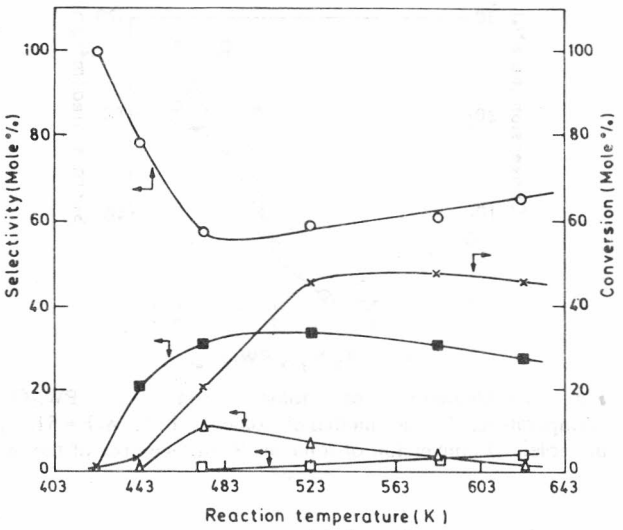


Fig. 3—Effect of reaction temperature on the conversion and the selectivity in toluene alkylation on $K_3PW_{12}O_{40}$ [methanol : toluene; 1 : 1, W/F = 76.4 g.hr/mole]; (○ xylene, ■ trimethylbenzene, × toluene, Δ tetramethylbenzene, □ benzene)

Nishi *et al.*[16] also proposed that the methyl carbocation formed on the heteropolyanion is the alkylating species. However, the surface concentration of the carbocation species controls the extent of alkylation as well as of conversion with respect to any one of the alkylated products. In order to probe this aspect, the effect of methanol to toluene ratio on selectivity and conversion was examined and the results are shown in Fig. 4. Toluene conversion shows a maximum at methanol to toluene ratio of 2 : 1. Selectivity of xylene passes through a minimum at this molar ratio and the selectivity of trimethylbenzene shows a maxi-

Table II—Effect of contact time on the conversion and the selectivity in alkylation of toluene on $K_3PW_{12}O_{40}$. [toluene:methanol; 1 :1]

Temperature (K)	W/F (g hr/mole)	Conversion (mole %)	Product selectivity (mole %)				Selectivity of xylene isomers (%)		
			benzene	xylene	trimethylbenzene	tetramethylbenzene	*p*	*m*	*o*
473	19.1	4.8	–	61.4	20.7	17.8	39.0	11.0	50.0
	29.9	11.1	–	43.4	36.4	20.2	37.0	12.8	50.2
	38.2	21.3	–	55.7	29.9	14.4	35.5	14.6	49.9
	76.4	21.2	–	57.3	31.1	11.0	30.0	15.1	54.9
523	22.0	5.9	–	62.6	18.1	19.3	33.0	19.0	48.0
	30.9	17.8	–	52.8	31.2	16.0	28.0	25.0	47.0
	51.8	26.3	1.8	51.4	35.0	11.5	25.0	24.0	51.0
	76.4	45.9	1.2	58.8	32.8	7.0	24.0	28.0	48.0
573	22.0	15.0	2.1	58.0	28.9	11.0	22.0	33.0	45.0
	30.9	21.2	2.1	56.6	35.5	8.8	20.0	35.0	45.0
	51.8	42.3	2.9	59.0	33.1	6.0	22.0	32.0	46.0
	76.4	47.6	3.4	60.6	31.6	4.3	19.0	38.0	43.0

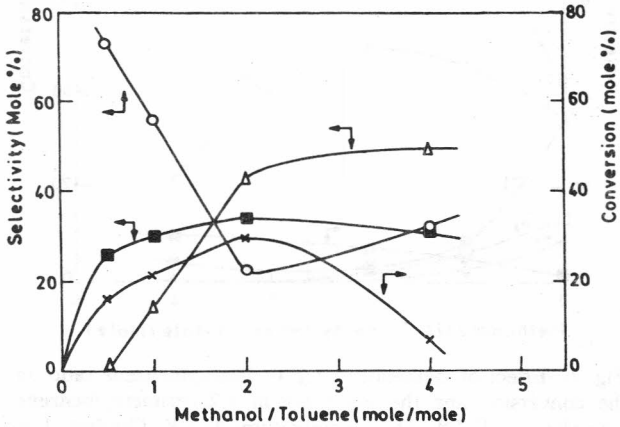


Fig. 4—Effect of methanol to toluene ratio on the conversion and the selectivity in toluene alkylation on $K_3PW_{12}O_{40}$ [Temperature; 473 K]; (○ xylene, ■ trimethylbenzene, × toluene, Δ tetramethylbenzene)

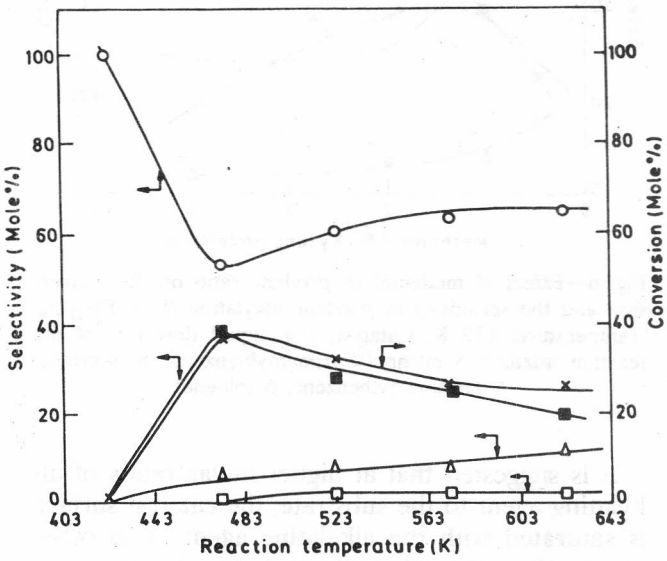


Fig. 5—Effect of temperature on the conversion and the selectivity in *p*-xylene alkylation on $K_3PW_{12}O_{40}$ [methanol : *p*-xylene; 1 : 1, W/F = 38.2 g hr/mole]; (○ trimethylbenzene, × *p*-xylene, ■ tetramethylbenzene, Δ toluene, □ pentamethylbenzene)

mum while that of tetramethylbenzene increases continuously with increasing methanol to toluene ratio. At methanol to toluene ratio greater than 3 : 1, the trace amounts of pentamethylbenzene have also been observed. This shows that the optimum ratio for the favourable formation of *tri*- and *tetra*-alkylated products is 2 : 1. After the initial alkylation, the products are desorbed, hence there is no increase in the selectivity of higher alkylated products. This probably means that the centres responsible for the adsorption of alkylating reagent and substrate are similar in nature and that the adsorption of alkylating agent in the form of CH_3^+ is preferred over the adsorption of the substrate.

In order to probe the reaction sequence further, alkylation of xylene as well as that of 1,2,4-trimethylbenzene was studied as a function of temperature (Fig. 5 and Table III) and as a function of molar ratio of the reactants (Figs 6 and 7). The trends of variation are similar to those observed in the alkylation of toluene (compare Figs 3 and 5 and Figs 4, 6 and 7) indicating that similar sites are involved in the alkylation of xylene, toluene and trimethylbenzene.

Table III—Effect of temperature on the conversion and product selectivity in the alkylation of 1,2,4-trimethylbenzene on $K_3PW_{12}O_{40}$ methanol : trimethylbenzene; 1 : 1, W/F; 51.8 g hr/mole]

Temperature (K)	Conversion (mole %)	Product selectivity (mole %)			
		xylene	trimethylbenzene	tetramethylbenzene	pentamethylbenzene
453	45.1	5.0	6.9	80.1	6.8
473	46.7	7.8	7.6	74.4	6.4
503	48.0	8.6	8.5	75.2	6.4
523	44.5	8.5	8.8	74.7	5.1

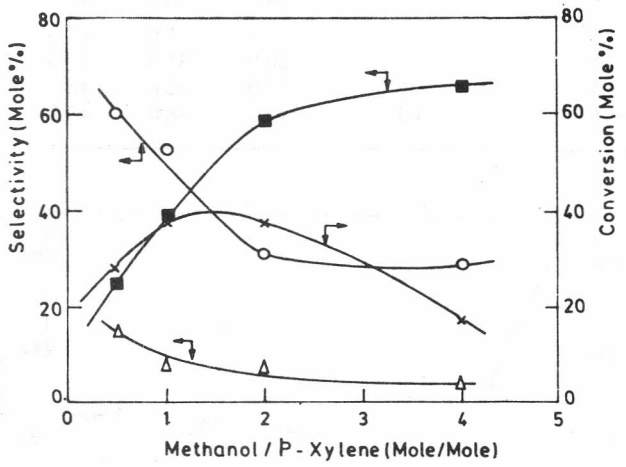


Fig. 6—Effect of methanol to *p*-xylene ratio on the conversion and the selectivity in *p*-xylene alkylation on $K_3PW_{12}O_{40}$ [Temperature; 473 K, Catalyst; 1 g, liquid flow rate of the reactant mixture; 5 ml/hr] (○ trimethylbenzene, × *p*-xylene, □ tetramethylbenzene, Δ toluene)

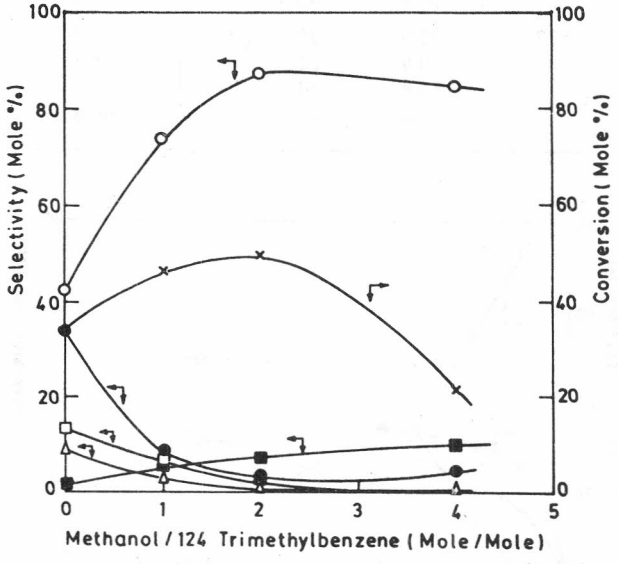
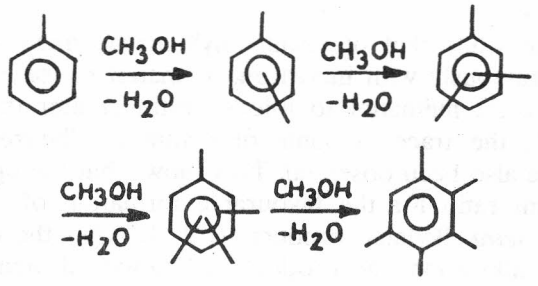


Fig. 7—Effect of methanol to 1,2,4-trimethylbenzene ratio on the conversion and the selectivity in 1,2,4-trimethylbenzene alkylation on $K_3PW_{12}O_{40}$ [Temperature; 473 K, Catalyst; 1 g, liquid flow rate of the reactant mixture; 5 ml/hr] (○ tetramethylbenzene, × 1,2,4-trimethylbenzene, ● xylene, □ 1,3,5- and 1,2,3-trimethylbenzene, Δ toluene, ■ pentamethylbenzene)

It is suggested that at higher molar ratios of alkylating agent to the substrate, the catalyst surface is saturated with the alkylating agent or in other words, the adsorption of alkylating agent is preferred over the adsorption of the aromatic substrates. Hence selectivity of polyalkylated products increases with increasing amounts of alkylating agent and both dealkylation and isomerisation processes are suppressed. This suggests that the centres responsible for the adsorption of alkylating agent and substrate are similar in nature and that the adsorption of alkylating agent in the form of CH_3^+ is preferred over the adsorption of substrate. Further, the similarity of data in the alkylation of all the three substrates indicates that the reaction sequence involves similar acive sites on the surface of the catalysts and the alkylating species is the methylcarbocation as proposed for the alkylation of toluene[16]. Hence, the reaction mechanism as shown in Scheme I for the successive alkylation of toluene on heterpolyoxometalates is proposed.



Scheme I

It is known that the higher alkylated products can be formed either by direct alkylation or by dealkylation route. It is usually difficult to distin-

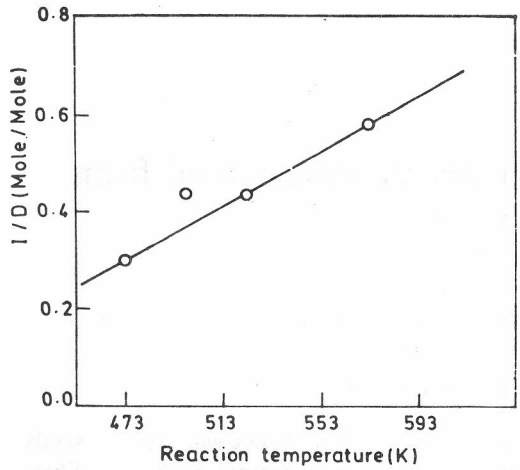


Fig. 8—Ratio of I/D from the reaction of 1,2,4-trimethylbenzene on $K_3PW_{12}O_{40}$ [W/F = 51.85 g.hr/mole]

guish between the dealkylation process and the transalkylation process. However, it is of value to examine the data generated in the dealkylation of trimethylbenzene as isomerisation (I) and dealkylation (D). In Fig. 8 the ratio* of I/D from the reaction of 1,2,4-trimethylbenzene on $K_3PW_{12}O_{40}$ is shown as a function of reaction temperatures. It is observed that with the increase in temperature, the isomerisation predominates over dealkylation. Similar results have been reported by Nishi and Moffat[23] for the reaction of 1,2-methylethylbenzene on $(NH_4)_4SiW_{12}O_{40}$. Hence, it can be suggested that alkylation always predominates over dealkylation process. This is due to the fact that the alkylating agent is activated on the surface of the catalyst in a facile manner as compared to the substrate. This again suggests that the adsorption of methanol and the formation of carbocation is preferred over the adsorption of substrate.

*Ratio of I/D was calculated as the ratio of the selectivity of isomerised products (1,2,3- and 1,3,5-trimethylbenzene) to that of the dealkylated products (xylene).

References

1 Keading W W, Chu C, Young L B, Weinstein B & Butter S A, *J Catal*, 67, **1981**, 159.
2 Young L B, Butter S A & Keading W W, *J Catal*, 76, **1982**, 418.
3 Derouane E G, in *Zeolites Science and Technology*, Vol. 80 (Martinus Nijhoff Publishers, Hague), **1984**, p.347.
4 Venuto P B & Landis P S, *Adv Catal*, 18, **1968**, 259.
5 Yahima T, Ahamed H, Yamasaki K, Katsuta M & Hara N, *J Catal*, 16, **1970**, 273 and 17, **1970**, 151.
6 Yashima T, Sato K, Hayasaki R & Hara N, *J Catal*, 26, **1976**, 303.
7 Sefick H D, *J Am Chem Soc*, 101, **1979**, 2164.
8 Itoh H, Hattori T, Suzuki K & Murakami Y, *J Catal*, 79, **1983**, 21.
9 Chen N Y, Keading W W & Dwyer, *J Am Chem Soc*, 101, **1979**, 6783.
10 Bhat S G T, *J Catal*, 75, **1982**, 196.
11 Coudurier G & Vedrine J C, *Pure Appl Chem*, 58, **1986**, 1389.
12 Kulkarni S J, Kulkarni S B, Ratnasamy P, Hattori H & Tanabe K, *Appl Catal*, 8, **1983**, 43.
13 Palekar M G & Rajadhyaksha, *Catal Rev Sci Eng*, 28, **1986**, 371.
14 King S T & Garces J M, *J Catal*, 104, **1987**, 59.
15 Okuhara T, Kasai A, Hayakawa N, Yoneda & Misono, *J Catal*, 83, **1983**, 121.
16 Nishi H, Nowinska & Moffat J B, *J Catal*, 116, **1989**, 480.
17 Bailor J C, *Inorg Synth*, 1, **1939**, 132.
18 Okuhara T, Nishimura T, Watanable H & Misono M, *J Mol Catal*, 74, **1992**, 247.
19 Misono M, *Catal Rev Sci Eng*, 29, **1987**, 269.
20 Misono M & Okuhara T, *Chem Tech*, **1993**, 23.
21 Highfield J G & Moffat J B, *J Catal*, 95, **1985**, 108; 98, **1986**, 245.
22 Angell C L & Howell M V, *J Colloid Interface Sci*, 28, **1968**, 279.
23 Nishi H & Moffat J B, *J Mol Catal*, 51, **1989**, 193.